

# STUDIES ON REMOVAL AND RECOVERY OF ZINC FROM WASTE WATER

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# STUDIES ON REMOVAL AND RECOVERY OF ZINC FROM WASTE WATER

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

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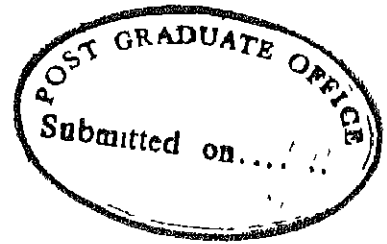
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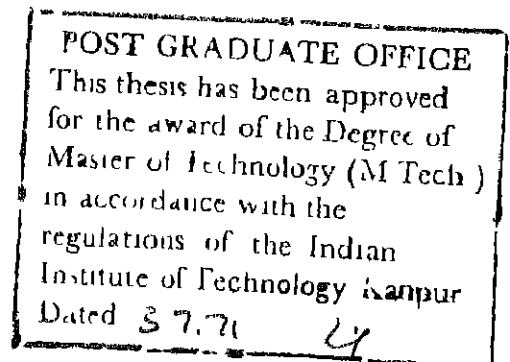
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JULY 1971



CERTIFICATE

This is to certify that the present work has been carried out by Sri M. Sivamony under my supervision and the work has not been submitted elsewhere for the degree.

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## SYNOPSIS

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by

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to the  
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Zinc is one of the valuable metals that is still being imported by our country. Considerable quantity of zinc as zinc sulphate is lost, from the waste waters of Viscose Rayon Industries. The study described in the Thesis is an attempt to remove zinc from the waste waters, since it is toxic to aquatic organisms and to recover as

much as possible by physical and chemical means as it is a valuable commodity.

Using a high capacity cation exchange resin, Zeo-karb 225, it was shown that almost complete removals of zinc could be achieved while 86.5% of the adsorbed zinc could be recovered. Compared to the studies on other types of resins available in literature, Zeo-karb 225 seems to have very high capacity, 1.8 kg/cft or 0.98 meq/ml. Chemical precipitation of zinc as hydroxide was also attempted using caustic soda and liquor ammonia. Even though liquor ammonia could be used, certain advantages were noticed with sodium hydroxide. These and related aspects have been discussed with special reference to not only removal, but also recovery of the zinc. Throughout the study the zinc was estimated by polarographic method.

## CHAPTER I

### INTRODUCTION

Among the various industries that are coming into prominence, the Viscose Rayon Industry is the one. Realizing the importance of this product the Government is liberalizing the import of raw material and is encouraging the development of viscose pulp for the Rayon Industry<sup>1</sup>. Industrialization is bringing not only prosperity on the one hand, but creating difficulties in the control of environmental pollution. Eventhough one is rather quick in blaming the industry, a proper understanding of the difficulties an industry is facing seems to be lacking. No industry wantenly intends to pollute the environment. In many cases, treatment of waste waters from the industries may be beneficial for the economy of the factory itself due to the possibility of recovering valuable materials including water, that may be reused, if not for economy, at least from the availability point of view. The demand on water is increasing both from domestic and industrial sectors. Resources are dwindling while demand is increasing. Intelligent industrial management is recognising the importance of recovery of water by removing the unwanted polluting materials from the waste. An economical method of treatment is of course essential for this purpose.

Zinc is one of the main constituent of rayon waste<sup>2,3</sup>. India is not self sufficient with regards to this valuable metal, zinc. The concentration of zinc in the composite waste from Indian industries vary from 6 to 18 mg/l<sup>2</sup>. To allow this concentration of the waste to go down the drain is an economic loss in the long run. A number of methods are used in foreign countries for the recovery of valuable zinc. Belonging to the group of heavy metals, zinc is known to exert toxic effect to the living systems. It had been noted that cattle were affected due to toxic concentrations of zinc coming from zinc smelters in the form of air borne dust<sup>4</sup>. The test samples collected around the vicinity of the foundaries showed a zinc concentration of 5 to 23%, in the air borne dust. The zinc seems to have affected the joints and cartilage from the bone, culminating in the paralysis of the animal.

Aquatic life is seriously affected with low concentrations of zinc. It has been reported by Jones<sup>5</sup> that depending on the species of fish, pH and characteristics of the water, as low a concentration as 0.3 mg/l of zinc is toxic to fresh water fish. However the U.S. Public Health has placed a limit of 5 mg/l as zinc for domestic water supplies<sup>6</sup>. Same value is reported in W.H.O. International and European Standards<sup>7,8</sup>. Water Quality Standards recommended

by the committee on Public Health Engineering Manual and Code of Practice constituted by the Ministry of Health, Government of India, March 1962 has recommended the permissible concentration of zinc as 5 mg/l. Russian standards seems to be more stringent in that they prescribed a value of 0.01 mg/l of zinc in the effluents<sup>9</sup>. Low concentrations do not seem to have no known adverse physiological effects on man<sup>10,11</sup>. It should be noted however that 2 mg/l of zinc imparts an unpleasant astringent taste to water<sup>12,13</sup>. Eventhough micro quantities of zinc are essential for animal and plant nutrition, higher concentrations prove toxic. Thus plants like orange was affected with 3 mg/l of zinc<sup>14</sup>, flax with 5 mg/l<sup>15</sup>, and water hyacinths with 10 mg/l of zinc<sup>16</sup>. Waste waters of zinc smelters in Udaipur Ore and Zawar mines were found to be toxic to blue green algae<sup>17</sup>. Thus it would seem that removal of zinc is essential to keep the ecological balance of streams unaffected by the waste waters from zinc mining operations, smelters, Plating Industries and Rayon Factories. It would be extremely useful not only to remove the toxic zinc from the waste liquids, but also to recover it for reuse in an industry. Thus these studies serve two purposes, that of removal and recovery. Studies have been carried out in advanced countries using

various methods for this purpose. Some work has been reported in India by CPHERI, Nagpur<sup>18,19,20</sup>. Using strong resins, with a different approach, some studies have been carried out on the removal and recovery of zinc from a local rayon industry, while the basic approach to the solution of the problem may remain similar. Each industrial waste has its own peculiar characteristics that have to be taken into account for a practical solution. It is in this light, the following results have to be viewed.

#### 1.1 Aim:

Removal and recovery of zinc from a viscose rayon industrial waste water.

#### 1.2 Scope:

The study is restricted to the use of acid wastes that solely contain the zinc. The methods of removal are restricted to ion exchange and chemical precipitation due to time constraints. A sensitive method of estimating zinc concentrations, that of polarographic method is used in assessing the concentration of zinc at various stages.

The pertinent literature connected with the study is described in the following pages.

## CHAPTER II

LITERATURE REVIEW2.1 Ion Exchange Process

When a mineral substance dissolves in water, it dissociates into electrically charged particles termed ions. The particles carrying a positive charge are known as cations, and those with a negative charge, anions. A solution of zinc sulphate, contain positively charged zinc cations and negatively charged sulphate anions. If such a solution is brought into contact with a suitable ion exchange material, the ions are exchanged so that some of the solution are taken up by the material and an equivalent number are transferred from the material to the solution. Ion exchange is thus a reversible exchange of ions between a liquid and a solid, no radical change being involved in the structure of the solid.

Matuskov<sup>21</sup> and Barboi<sup>22</sup> worked on ion exchange method of absorbing zinc from viscose waste water. The Industrial Rayon Corporation, Brit.,<sup>23</sup> used an ion exchange resin Dowex 50 x 12 to recover zinc from rayon wastes. The zinc is eluted with 20%  $H_2SO_4$  and 2.8% zinc sulfate solution is recovered.

Zagari<sup>24</sup> investigated the cation exchanges, but from the view point of bubbling layer. Konganovskii<sup>25</sup> studied the use of cation exchange resin in a fluidized bed. A three unit column is used with a sulphonated coal cation exchanger resin for removal of zinc. The exchanger gives 99% zinc removal. The resin is regenerated with a 3% solution of sodium sulfate. Valkhausky<sup>26</sup> and Mevkulova<sup>27</sup> also studied the use of ion exchange resins for the recovery of zinc.

Stempkovskaya<sup>28</sup> worked on the use of a strongly acidic cationic resin KU. 1. The zinc content in the effluent was reduced to 0.01 mg/l<sup>28</sup>. A semitechnical pilot plant was described by Stempkovskaya in which cation exchangers reduced the zinc concentration from 60 mg/l to 1 mg/l<sup>29</sup>. Shimko<sup>30</sup> extracted carbon bisulfide by an adsorption desorption method and then used cation exchange resin for the zinc removal. Sixty tons/year of zinc sulfate was returned into production. Straobinets<sup>31</sup> combined a cation anion method of zinc removal.

Kantwala and Tomlinson<sup>32</sup> studied the recovery of zinc by using a cation exchange resin. It is stated that the recovery efficiency was 99% in the first run and it was decreased to 64% in the fourth run.



Marinich<sup>33</sup> & Aston<sup>34</sup> also studied the use of ion exchangers for the recovery of zinc from rayon wastes. Bakuni and Bopardikar<sup>19</sup> studied the use of both indigenous and imported resins for the recovery of zinc. Sastri and Khare<sup>20</sup> made a comparative study on recovery of zinc by ion exchange method and chemical precipitation method. The indigenous cation exchange resins were found to have a capacity of 0.088 to 0.194 kg of zinc per cft of resin. The indigenous cation exchange resins used are Tulsin 14 and Tulsin 42.

## 2.2 Chemical Precipitation

Several authors<sup>37-41</sup> worked on the neutralization of acidic viscose rayon waste. Matsnev<sup>42</sup> reported on viscose waste treatment for coagulation, then filtration or flotation. The best purification was obtained by flotation after the chemical treatment. Popp<sup>43</sup> worked out a tentative full scale scheme for alkaline flocculation based on extensive laboratory investigations. Agranonik<sup>44</sup> suggested screening, neutralization with lime, clarification with a fluidized bed and final biological purification. Mongait and Fisherman<sup>45,46</sup> recommended the use of sodium carbonate to precipitate zinc as zinc carbonate. Zinc carbonate is filtered out and sodium bisulphide is added for final zinc stripping.

Mongait<sup>47</sup> suggested addition of lime to adjust pH 9 to 10 and then sodium bi sulfide addition to give good zinc removal.

Barochina<sup>48</sup> worked on the combined treatment of zinc waste and hydrogen sulfide removal simultaneously. A zinc removal of 90 to 95% was obtained with a zinc hydrogen sulfide ratio 3 to 4. Matsnev<sup>49,50</sup> has carried out considerable work on the removal of CS<sub>2</sub>, H<sub>2</sub>S and zinc by flotation.

Lerazynski<sup>51</sup> worked on the chemical coagulation of viscose wastes. After neutralizing by adding alkaline and acidic wastes together, alum was added. This treatment was claimed to be more successful than lime precipitation. Stempkovskaya<sup>52</sup> worked on other flocculants like activated silica, sodium silicate and polyacrylamides. The polyacrylamides gave the best results at the lowest cost. Popp<sup>53</sup> continued his work on the effect of chemical precipitation and settling using mixing for neutralization, aeration for CS<sub>2</sub> and H<sub>2</sub>S removal and CaO for the zinc removal.

Barochina<sup>54</sup> used a counter current absorption tower to remove zinc and H<sub>2</sub>S in one step. The H<sub>2</sub>S laden air was blown into the bottom of the tower while the zinc containing waste trickled down from the top. The optimum pH was found to be 10.

Several authors<sup>55-58</sup> worked on the soda sulfate method of zinc removal. Fishman<sup>59</sup> studied the use of soda sulphate for 100% removal of zinc. The method consisted of addition of sodium carbonate solution to pH 4 to 4.5, blowing with CO<sub>2</sub> in a degasifier, raising again the pH to 8.5 to 9.5 to precipitate Zn<sub>3</sub>CO<sub>3</sub>(OH)<sub>4</sub>. Final zinc removal by Na<sub>2</sub>S, was accomplished and followed by sand filtration. Zakharina<sup>60</sup> discussed a combined treatment of vent gas and waste waters from viscose rayon production. Matuskov<sup>61</sup> worked on the use of a contact clarifier plus chemical precipitation.

Skrylev<sup>62</sup> removed zinc by successive treatment with solutions of Na<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub> and NaOH. The final separation of zinc was carried out by flotation.

A neutralization procedure for recovery of zinc from viscose rayon production waste was described by Saxena and Chakraborty<sup>63</sup>. Chakraborty<sup>64</sup> studied on chemical precipitation by using lime and sodium hydroxide for the recovery of zinc for reuse. Zhukov<sup>65</sup> described the use of Na<sub>2</sub>S for zinc removal. Kaeding<sup>66</sup> worked on precipitation of alpha cellulose and zinc by using NaOH.

Hill<sup>67</sup> reviewed the waste control programme at American Enka. The zinc was precipitated as zinc hydroxide which could be reused. The system recovered 90% of zinc.

## CHAPTER III

### MATERIALS AND METHODS

A brief description of the manufacturing process is very essential for knowing the source and characteristics of the waste. A flow through diagram of the manufacturing process is given in Figure 1.<sup>3</sup>

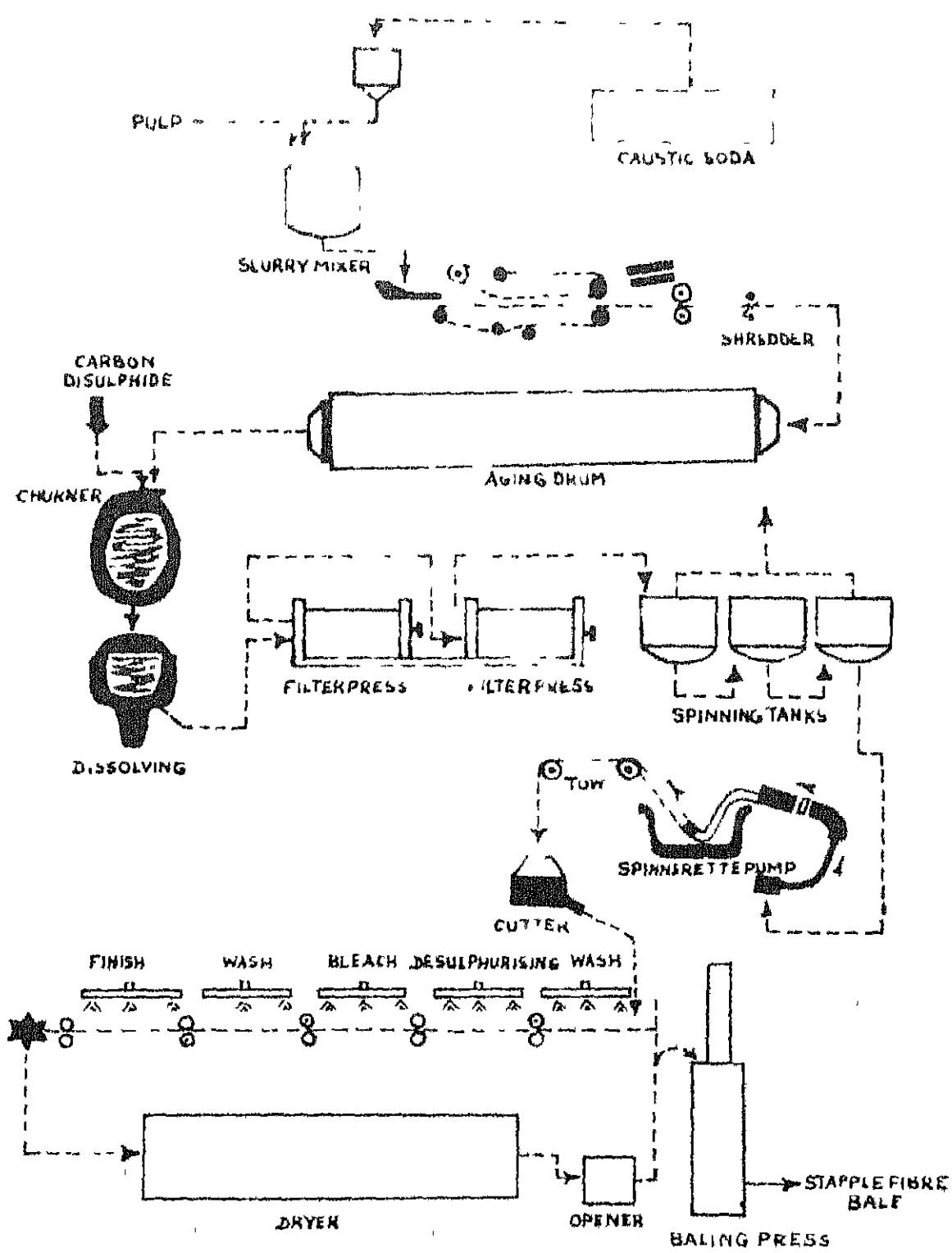
#### 3.1 Manufacturing Process of Viscose Rayon

The viscose process in general consists of the following steps.

Sheets of cellulose are immersed in caustic soda solution (18%). The hemicellulose dissolves in it and alfa cellulose remains insoluble.

The sheets are then pressed to a predetermined weight and the pressed out soda is either reused or sent to a dialyser for recovery. The alkali cellulose ~~sheets~~ are shredded into crumbs, aged for a specified period at a given temperature.

The aged crumbs are then xanthated by addition of carbonbisulphide. The xanthated crumbs are dissolved in a dilute caustic soda solution (6 to 7%) forming a viscous red orange solution about the consistency of molasses called viscose.



**FIG 1 FLOW SHEET OF VISCOSE RAYON MANUFACTURE**

The viscose is aged at constant temperature for the proper length of time during which it is filtered through a series of progressively finer filters and evacuated to remove air.

After aging, the viscose is pumped through the final polishing filter and extruded or "spun" through a number of fine holes into an acid bath where the cellulose is coagulated into filaments. A number of filaments form a thread. The coagulation bath contains sulphuric acid (8 to 10%) sodium sulfate (13 to 20%) and zinc sulfate (0.5 to 1.2%) in widely varying ratios depending upon the characteristics of the desired product.

During the spinning operation the coagulation bath is diluted with water from viscose, lowered in acid concentration and enriched in sodium sulfate from caustic in viscose.

The spent bath is corrected to proper concentration and reused. Part of it is sent to a reclaim operation where excess water and sodium sulfate are removed by evaporation and recrystallisation, then returned into the bath make up tank. The sodium sulfate recovered is usually sold as "Glaubers" salt or converted into anhydrous and sold.

The rayon leaving the coagulation bath carries some of the bath with it and must be further processed. During the spinning operation sulphur is precipitated on the rayon fiber which is removed by treatment with an alkaline sodium sulphide solution which dissolves the sulfur and forms polysulphide. The yarn is then washed with water and further undergoes a number of processes which include bleaching, washing with dilute acid and detergents and finally with plain water. The yarn is then dried, conditioned to proper moisture content and packaged for sale.

### 3.2 Sources of Waste Water

Process waste waters is generated at several points in the production viscose Rayon. Equipment washing and chemical recovery operations are additional sources of contaminants. Cellulose, caustic soda, sulphur products, sulphates sulphuric acid and zinc sulphate are lost in varying amounts to the sewers. The operation may vary according to product demand and routine maintenance needs. So waste water generation is continuous, but variable in quantity and quality.

However the waste water produced by a viscose rayon factory is mainly divided into two types, acidic and

alkaline. The acidic wastes are generated from spinning and after treatment units. Alkaline wastes are the wastes coming from dialyzers ripening department, desulphuring plant, carbon bi sulphide plant etc.

### 3.3 Characteristics of the Wastes

The characteristics of the wastes from viscose rayon factories are found to vary, very widely in nature and contents. The quantity of composite liquid wastes produced from a viscose rayon industry is found to vary from 0.15 MGD to 0.5 MGD per ton of rayon produced<sup>20</sup>.

The main source of zinc is the acidic viscose rayon waste. The acidic waste for the experimental work was obtained from a local viscose rayon factory and the characteristics of the waste is given in table 1.

### 3.4 Experimental Set Up For Ion Exchange Process

The experimental set up is shown in Figure 2. The ion exchange column used is 1.2 metres long and 2.5 cm in diameter. Glass wool and glass beads are used to support the resin. The volume of resin used is 150 ml. The waste water was pumped to an aspirator bottle of 10 litre capacity kept above the column. The flow of the waste was by gravity to the column and it was regulated by means of



TABLE 1

CHARACTERISTICS OF THE ACIDIC RAYON WASTE

pH	2.8
Total Solids	2500 mg/l
Suspended Solids	80 mg/l
Acidity	300 mg/l
Zinc	360 mg/l
Sulphates	1500 mg/l
Sulphides	Nil
Chlorides	30 mg/l
C.O.D.	300 mg/l
Specific Conductance	$3.5 \times 10^{-3}$ mhos.

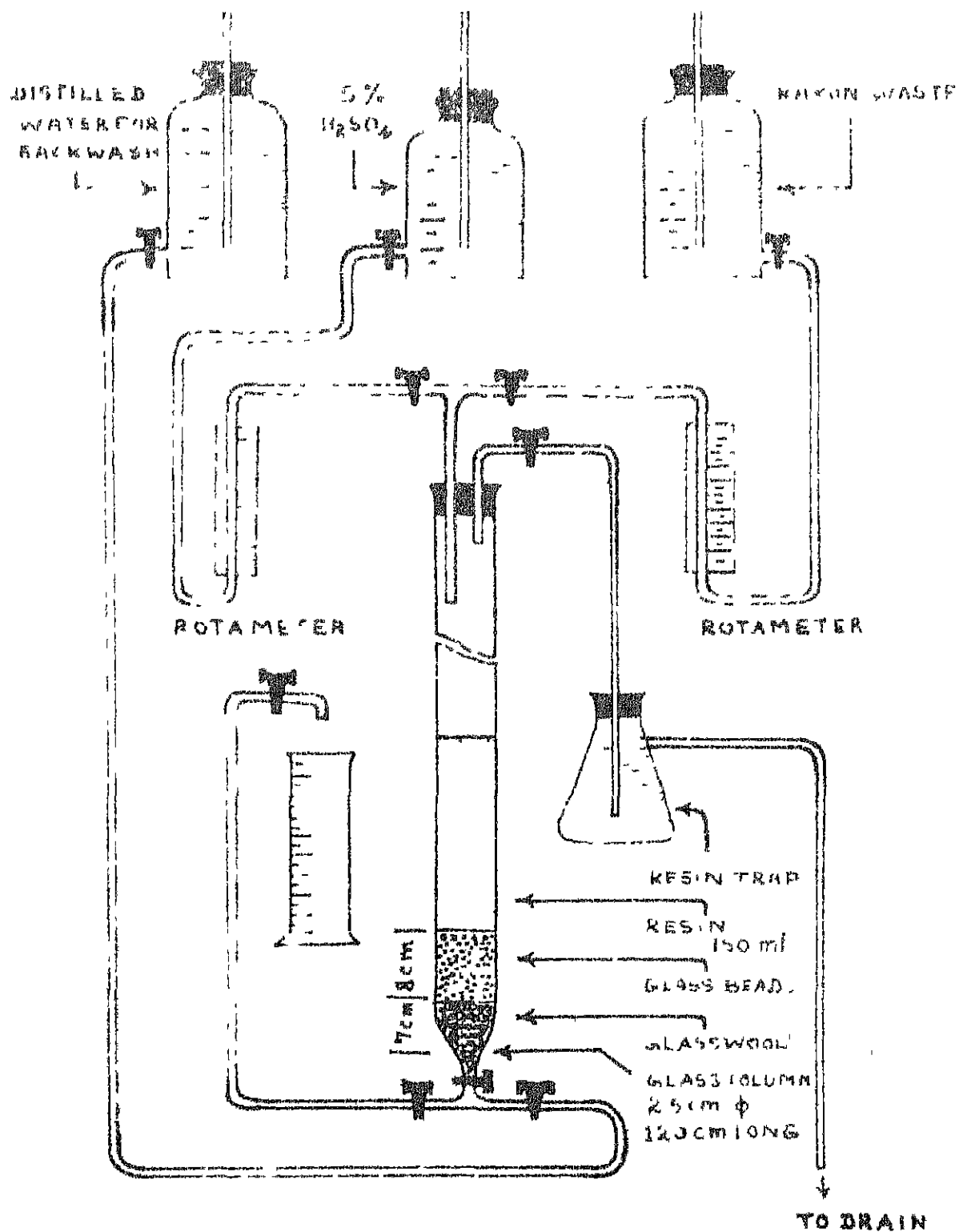


FIG. 2 EXPERIMENTAL SET UP FOR ION EXCHANGE

a Rotameter\* and constant flow device. A constant volume of 150 ml was maintained on the top of the resin beads during the run.

The eluant (5% sulfuric acid) was kept in a 5 litre aspirator bottle connected with a constant flow device above the column. The eluant was allowed to percolate through the column during the elution process through a Potameter. The back washing was done by means of distilled water, kept in an aspiratory bottle with constant flow device above the column. The wash water is led from the top of the column through a tube carried in a rubber lining, into a resin trap, and thence to the drain.

The treated waste was collected through a side arm. The outlet was 5 cm above the top of the resin bed. This was to avoid the possibility of water level going below the top of the resin bed. Otherwise air will enter the bed, which may lead to erraneous results.

### 3.5 Characteristics of the Resin Used

The resin used was Zeo-karb 225. Zeo-karb 225 is a strongly acidic unifunctional, cross linked polystyrene cation exchange resin in bead form, containing sulphonic acid groups.<sup>35</sup> Zeo-karb 225 is used both for sodium exchange

(softening) and for hydrogen exchange (demineralising) and

\* Manufactured by Instrumentation Engineers, Hyderabad.

is also used in a large number of process applications.

### 3.5.1 Physical Characteristics

Shipping weight	848 kg/m <sup>3</sup> in Na <sup>+</sup> form
Grading	0.3-1.2 mm (-14 + 52 British Standard mesh)
Effective size	0.4 mm
Uniformity coefficient	about 1.4
Voids	approximately 40%.

### 3.5.2 Chemical Characteristics

#### Stability

- (a) Thermal
  - H<sup>+</sup> form-stable upto 120°C
  - Na<sup>+</sup> form-stable upto 140°C
- (b) pH range 0-14
- (c) In oxidising agents Resistance to chlorine is dependent on the temperature of the feed water. For temperature up to 15°C the free chlorine must not exceed 1 ppm. For temperatures between 15°C and 30°C free chlorine must not exceed 0.5 ppm. For water temperatures above 30°C no free chlorine should be present. Free

chlorine in excess of the amounts stated should be eliminated by sodium sulphite dosing.

(d) In reducing agents Good

(e) In organic solvents Good

3.5.3 Total Capacity 100 g.  $\text{CaCO}_3$  per litre (2 gram / eq. per litre)

### 3.6 Pre-treatment of Resin

Before any examination or characterization of an ion exchange resin can be performed, the resin must be pretreated so that it is in the proper form.<sup>36</sup>

About 400 ml Zeo-karb 225 is taken in a 1 litre beaker. The resin is stirred well by adding water and soaked for 1 hour. The slurry is decanted into the ion exchange column. The resin ~~settles~~ and forms a bed supported on the glass wool and glass beads. The column is backwashed at 100% bed expansion until a clear backwash effluent is obtained. The resin bed is then permitted to settle and drain the excess water. The volume of the resin is noted. The back wash is repeated and allowed to drain. The volume of the resin is noted again.

The resin is treated with about 5 bed volumes of 10% NaCl solution and then rinsed with distilled water.

The resin was then regenerated with 5 bed volumes of 5%  $H_2SO_4$ . Finally the resin was washed free of any excess regenerant or chloride. The whole cycle was repeated thrice. This sort of cyclic treatment is necessary for those strong electrolyte resins, requiring the analysis of field samples<sup>3,6</sup>

The sample is then dried on a Buchner funnel with very mild suction applied until the free or excess water is removed. The treated resin is then stored in glass stoppered bottles.

### 3.7 Method of Analysis of Zinc

The zinc content of the waste was analyzed by means of a Sargent Fast Sweep Polarograph Model F.S.

The principle is based on the unique properties displayed by an electrolytic cell consisting of a non polarizable electrode in the form of a mercury drop falling from a capillary and containing small amounts of electro reducible or electrooxidizable material.<sup>68</sup> When an increasing electromotive force is impressed across such a cell and the resulting current plotted as a function of the applied voltage, a curve is obtained whose extension along the current axis is directly related to the concentration of trace material and whose inflection

point is located at a voltage characteristic of that material.

Since most electroreducible substances have different decomposition potentials, it is possible to measure several constituents in the same operation. Further the electrolysis involves only a small amount of the sample that which is in contact with the mercury electrode.

<sup>69</sup>  
The Fast Sweep Polarograph is designed for the measurement of current voltage curves using the techniques of Fast Sweep Polarography. These methods are straight forward extensions of "classical" polarography with two modifications. First a stationary working electrode is used in place of the dropping mercury electrode and second, the voltage is scanned at a much faster rate than in classical polarography. These two changes result in current voltage curves which are much different in appearance from conventional polarograms.

The curve obtained by this method for a solution containing zinc is shown in Figure 3. The reason for the peak shape (which is related to the maxima appearing in conventional polarograms) is that the slow process of diffusion is unable to supply reducible material to the electrode fast enough to keep up with the rapidly increasing potential, so that a steady state is never attained. It

$$I = 0.732 F \frac{1}{cm} \frac{1}{3} \frac{1}{s}$$

$D = \text{diffusion Coe}$   
 $C = \text{molar conc}$   
 $m = \text{mass of mercury flowing per sec.}$

CURRENT IN MICROAMPERES

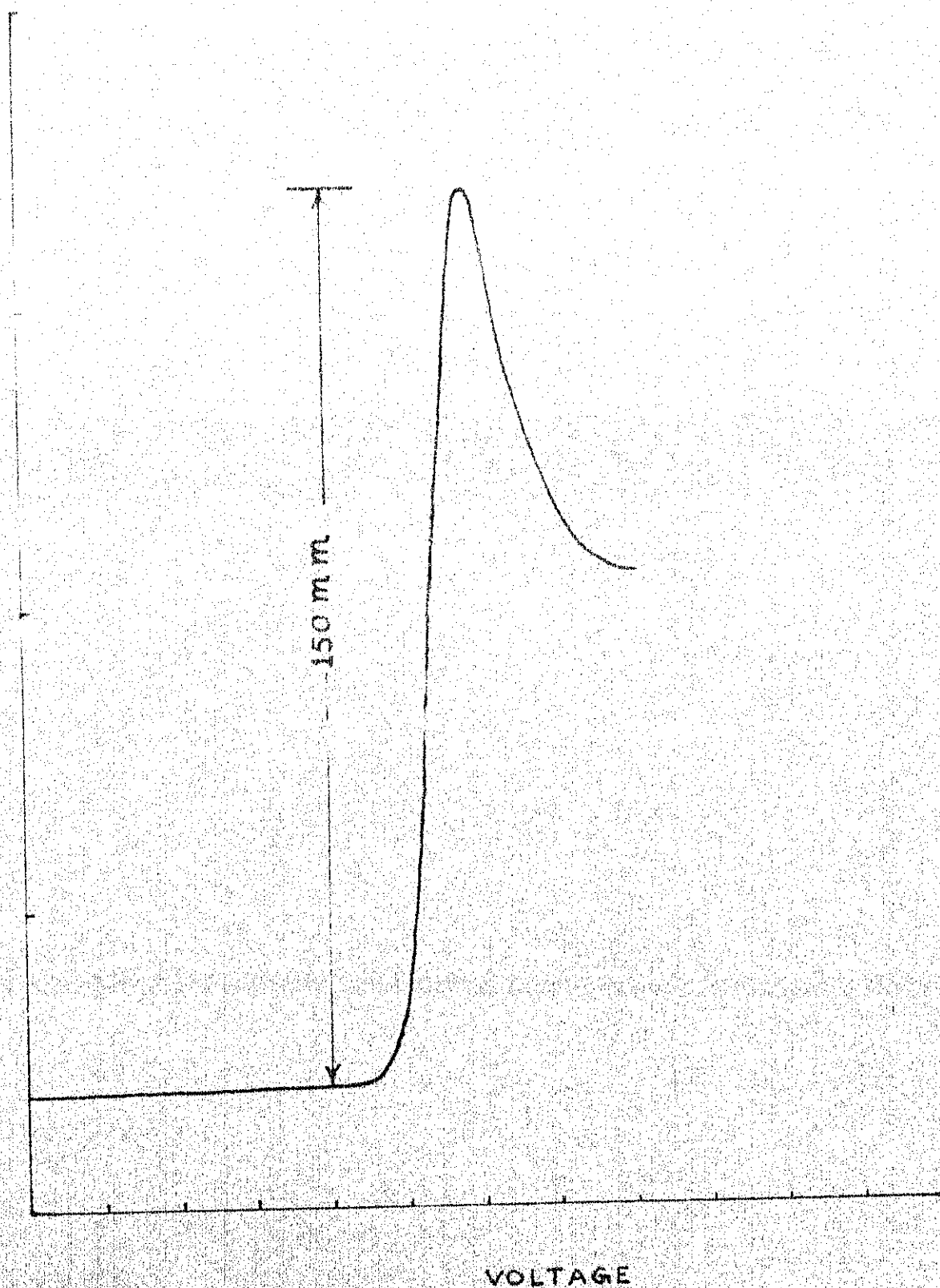


FIG: 3. TYPICAL POLAROGRAM OF ZINC FOR A CONCENTRATION  
OF 62 mg/l [SENSITIVITY = 0.100  $\mu$ A/mm]



can be shown mathematically that  $E_s$ , the summit potential is related to the half wave potential.

The method of Fast Sweep Polarography has several advantages on conventional polarography. First at reasonable rates of voltages scan (15 to 50 mv/sec) the charging current on a stationary electrode is about ten fold lower than on a dropping mercury electrode of the same area. This means that analysis can be made at concentration levels about one order of magnitude lower than when using a dropping mercury electrode. The second advantage is that the analysis can be done much more rapidly, since the entire current voltage curve is obtained in 60 seconds or less, compared to 10 minutes for a conventional polarogram.

The technique of Fast Sweep Polarography has been used with various electrodes viz. mercury pool electrodes, platinum wire electrodes and hanging mercury drop electrodes. From the analytical point of view, the most useful of these electrode systems is the hanging mercury drop electrode (HMDE) for work in cathodic potential range.

The polarographic method given in Standard Methods<sup>70</sup> is modified for the analysis of zinc. This was necessary because about 100 ml of the sample was needed in the case of Fast Sweep Polarograph as against 7.5 ml in the case of conventional polarograph.

The following procedure was adopted to estimate zinc by the Fast Sweep Polarograph.

- (1) Take a sample size of 100 ml in a 250 ml flask.
- (2) Evaporate to dryness after adding 3 ml of concentrated nitric acid.
- (3) Add 2 ml of concentrated hydrochloric acid and evaporate to dryness.
- (4) Treat the residue with 0.5 ml of hydrochloric acid.
- (5) Add 100 ml of distilled water.
- (6) Add a few crystals of sodium sulphite and warm the flask.
- (7) Add 13 ml of concentrated ammonium hydroxide and mix well.
- (8) Add 13 ml of Ammonium Carbonate solution and mix well.
- (9) Add 2.5 grams of Sodium Sulphite and allow the sample to stay for 30 minutes.
- (10) Transfer the solution to the polarographic cell.
- (11) Record the current voltage curve in the voltage range of -0.8 V to -2 V. The recording can be stopped just after obtaining the peak.

Experiments were done with and without evaporation of the sample. It is found that the evaporation step was

not necessary in the analysis of zinc from viscose rayon waste, as the results obtained in both the cases were found to be almost the same. So further experiments were done without evaporation.

A calibration curve is presented in Figure 4. From this graph concentration of zinc upto 100 mg/l can be estimated directly. For concentrations exceeding 100 mg/l suitable dilutions are necessary before polarographing.

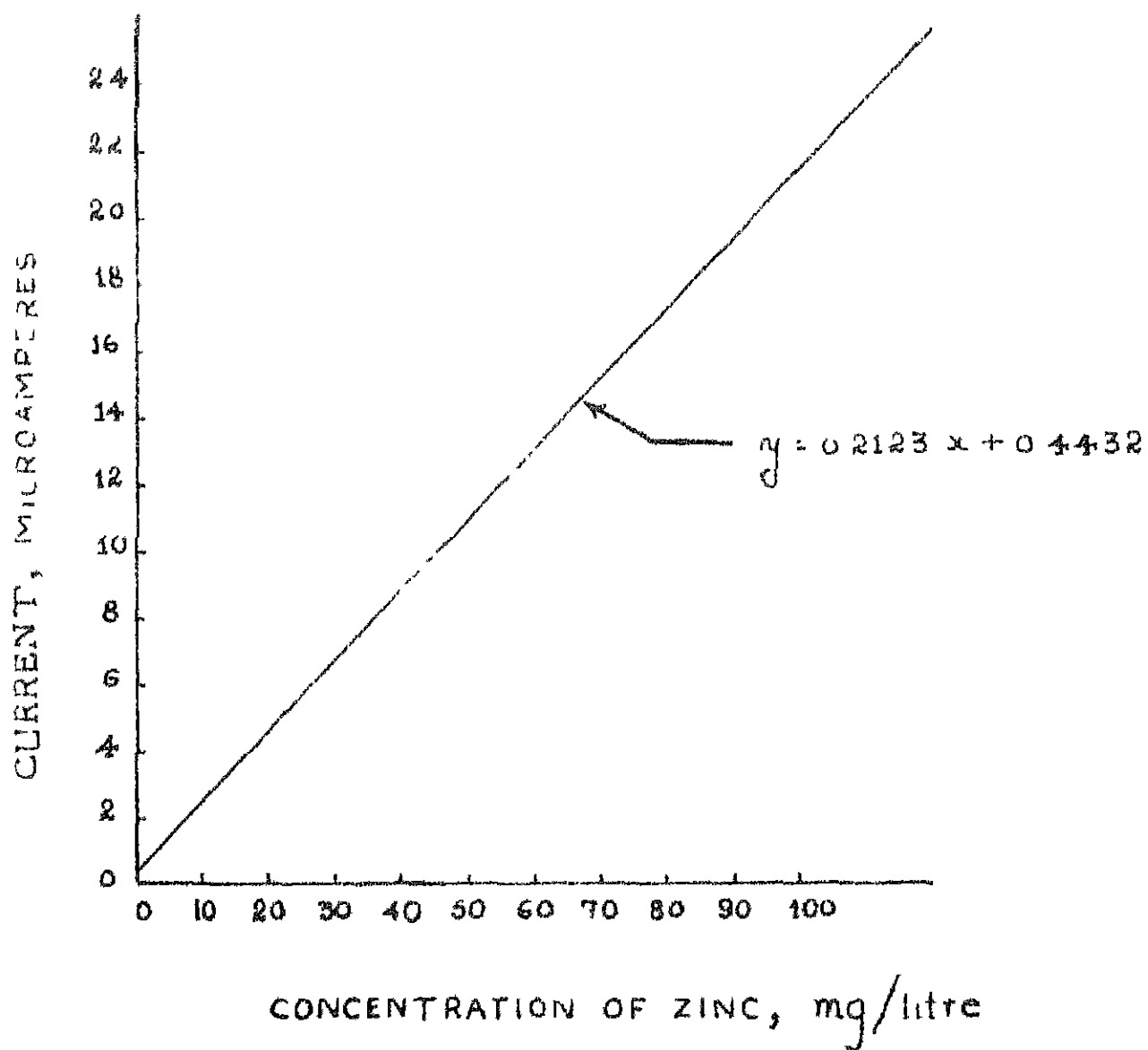


FIG:4 CALIBRATION CURVE FOR ZINC.

"FAST SWEEP POLAROGRAPH"

## CHAPTER IV

### EXPERIMENTS

The study is aimed at removal as well as recovery of zinc as mentioned earlier. Two major methods are used to achieve this purpose. One is the ion exchange method using a strong cation exchange resin in the hydrogen form and the second being the chemical precipitation. These are described below.

#### 4.1 Ion Exchange Resin

The characteristics of the resin and the details of the experimental set up are given in the previous chapter. Before using the actual rayon waste water collected from the factory, it was thought advisable to use a synthetic rayon waste whose composition can be controlled and checked for the purpose of evaluating the performance of the resin without interfering from any unknown chemical or organic materials from the natural waste that cannot be normally analyzed.

Ion exchange operations consist of backwashing, regeneration, rinsing and exhaustion. These operations have been conducted with the resins and the experiments have been repeated at least two times. A set of experimental

data with synthetic waste, and acidic rayon waste are given below.

#### 4.1.1 Synthetic Waste:

A synthetic waste having a zinc content of about 200 mg/l and a pH of 2.2 is allowed to percolate through the resin bed of 300 ml volume at the rate of 200 ml/minute/litre of resin (0.2 bed volume/minute)<sup>71</sup>. The treated waste was collected in one litre quantities and analyzed for presence and concentration of zinc. The flow of the waste through the column was stopped when the concentration of zinc in the effluent reached a value of 12.0 mg/l, about 5% of the initial concentration. The "Break through" curve of the synthetic waste is presented in Figure 5.

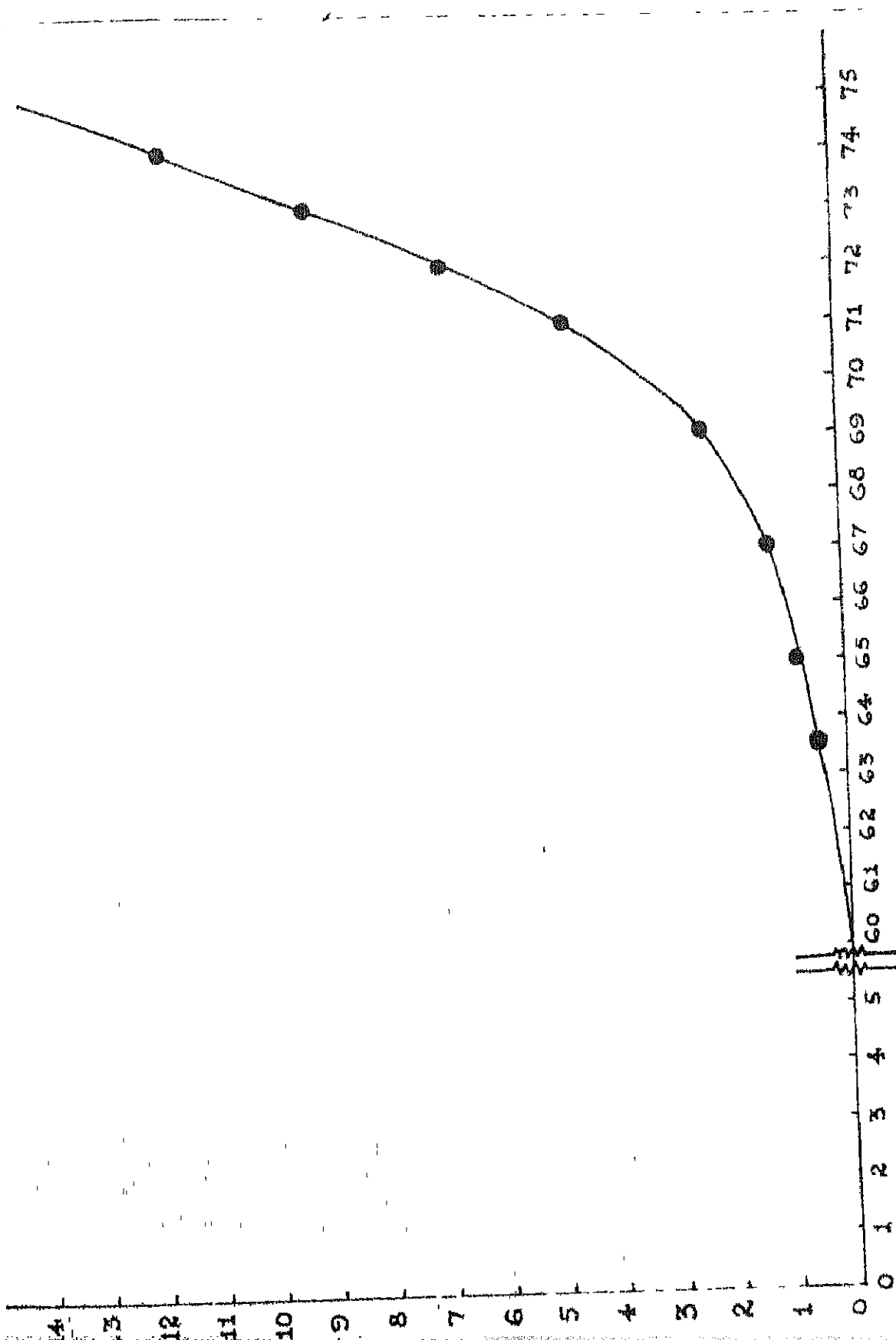
#### 4.1.2 Acidic Rayon Waste

In this study the volume of the resin was reduced to <sup>150</sup>~~300~~ ml, due to the difficulty in obtaining and storing huge quantity of wastes. The waste was allowed to percolate at the rate of 200 ml/minute/litre of resin (0.2 bed volume/minute). The effluent was collected in 1 litre lots and analyzed for zinc, pH\*and Specific Conductance\*\* The experimental results are shown in Figure 6.

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\* Beckman pH Meter

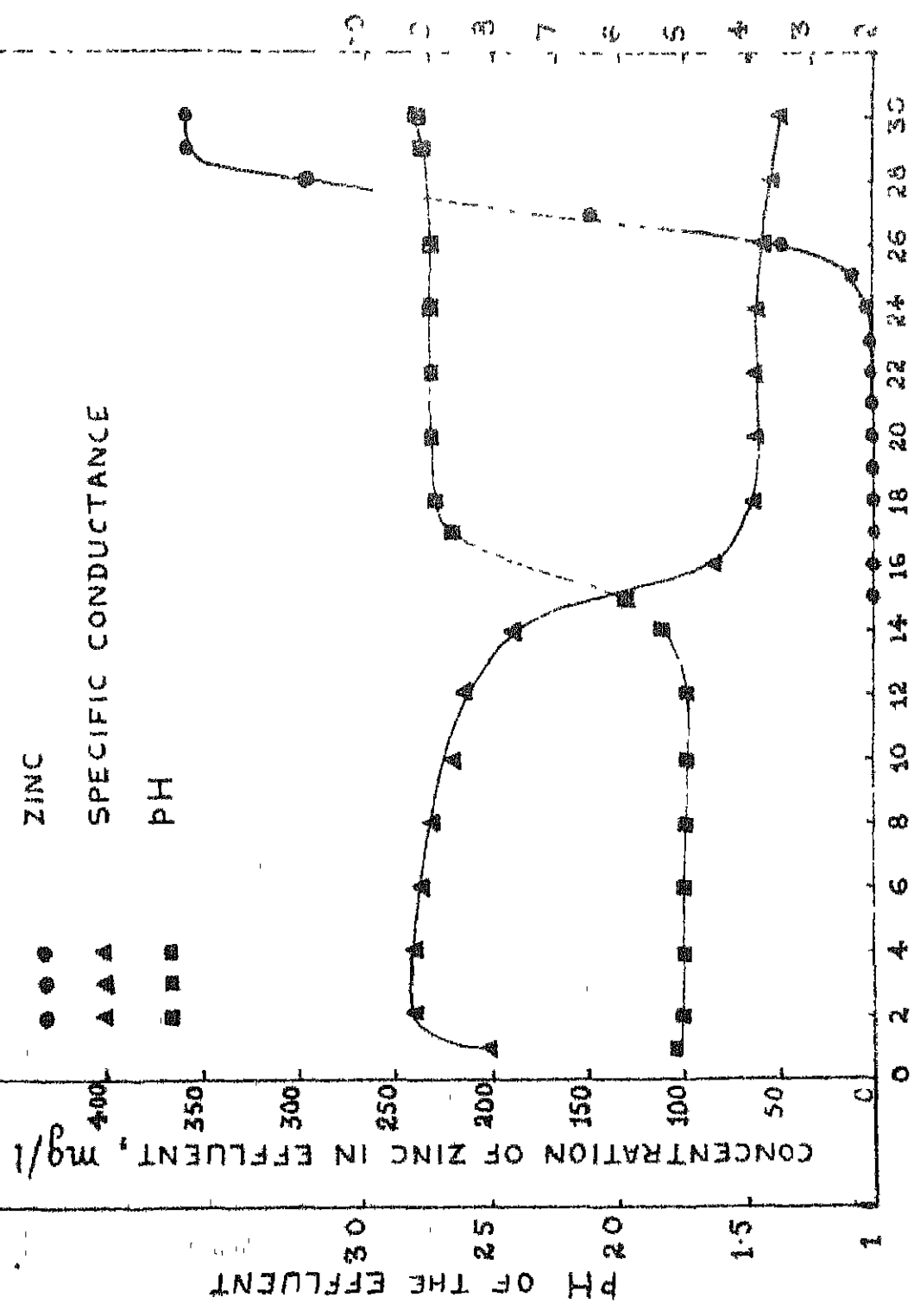
\*\* Wiss-Techn-Werkstätten, Weiheim Obb. Type LBR/B  
Made in Germany.



VOLUME OF SYNTHETIC WASTE, LITRES

FIG 5 BREAKTHROUGH CURVE FOR SYNTHETIC WASTE

THE EFFLUENT CONDUCTANCE,  $10^{-3} \times \text{mhos}$



ACIDIC RAYON WASTE, LITRES

FIG. 6 EXHAUSTION CURVE FOR ACIDIC RAYON WASTE

CONTAINING ZINC



After exhaustion, the resin bed was "sweetend off" and backwashed using distilled water. The elution was done using 5% sulfuric acid. The acid was allowed to percolate through the column at a flow rate of 5 ml/minute. The contact time allowed was 30 minutes.<sup>72</sup> The eluate was collected in different quantities and analyzed for zinc. The flow of the eluant was stopped when the concentration of zinc in the eluate was about 6 mg/l. The elution curve is presented in Figure 7.

#### 4.2 Chemical Precipitation

Perhaps one of the widely used methods for removal of zinc is the process of chemical precipitation. The solubility of compounds of zinc is given in Table 2. It can be seen that zinc hydroxide is one of the compounds having low solubility. For removal of zinc one might use lime precipitation where as recovery of zinc from the precipitated sludge is a difficult process because of the impurities as well as hydroxide of lime present in the precipitate. In the present study, the use of Sodium hydroxide has been tested and compared with Ammonium hydroxide.

Actual acid rayon waste, that has been used in the previous experiments of ion exchange has been adjusted

to various pH values with different quantities of Sodium hydroxide or Ammonium hydroxide. The flocculation and precipitation of hydroxide of zinc is assisted by stirring the mixtures after the addition of alkali for 15 minutes at 60 rpm in the conventional laboratory flocculator. The precipitate was allowed to settle for half an hour before a clear liquid from within one inch from the surface is taken out and analyzed for residual zinc. The volume of the sludge produced in the various operations is also noted. Significant data on these experiments is presented in Figures 8 and 9.

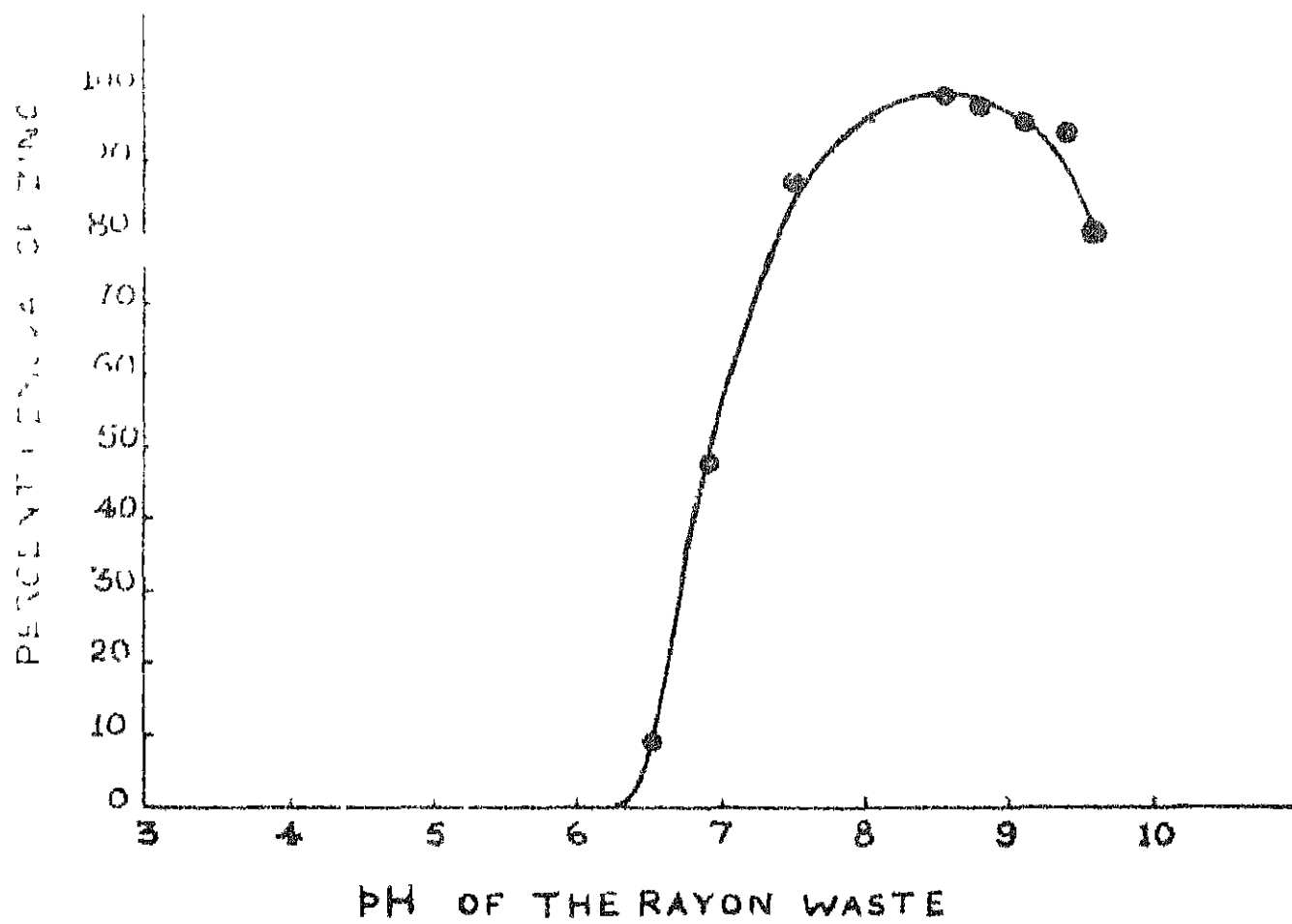


FIG 8 RECOVERY OF ZINC USING  $\text{NH}_4\text{OH}$

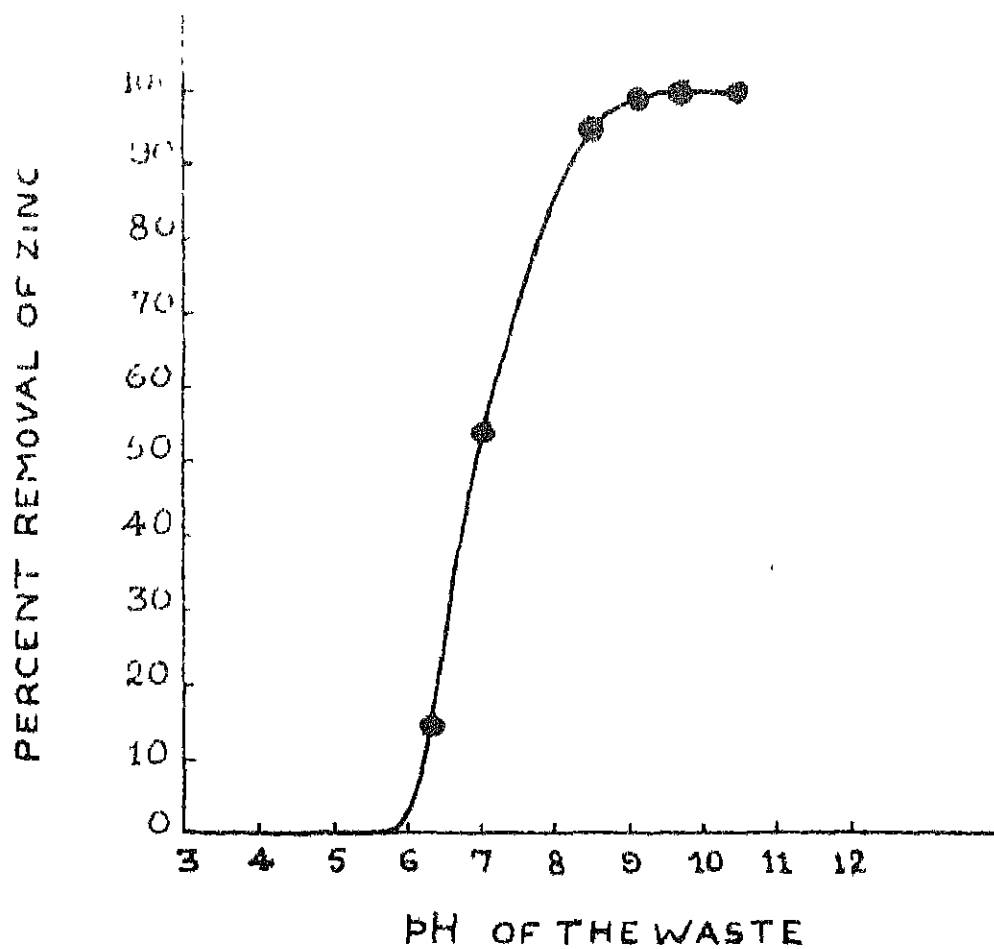


FIG: 9. RECOVERY OF ZINC USING NaOH

TABLE 2

SOME INSOLUBLE COMPOUNDS OF ZINC<sup>73</sup>

NAME OF THE CHEMICAL	FORMULA	SOLUBILITY (gms/100 ml)	
		IN COLD WATER	IN HOT WATER
Zinc Aluminate	$\text{ZnAl}_2\text{O}_4$	1*	i
Zinc Orthoarsenate	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	1	1
Zinc Arsenide	$\text{Zn}_3\text{As}_2$	i	..
Zinc Chromate	$\text{ZnCrO}_4$	i	..
Zinc Ferrocynide	$\text{Zn}_2\text{Fe}(\text{CN})_6$	i	i
Zinc Ferrocynide	$\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	1	i
Zinc Formaldehyde Sulfoxylate	$\text{Zn}(\text{OH})\text{HSO}_2\text{CH}_2\text{O}$	1	1
Zinc Oleate	$\text{Zn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$	1	..
Zinc Orthophosphate	$\text{Zn}_3(\text{PO}_4)_2$	i	i
Zinc Pyrophosphate	$\text{Zn}_2\text{P}_2\text{O}_7$	i	i
Zinc Phosphide	$\text{Zn}_3\text{P}_2$	1	..
Zinc Sulphide	$\text{ZnSH}_2\text{O}$	1	..

SOME COMPOUNDS OF ZINC WITH LOW SOLUBILITIES

Zinc Carbonate	$\text{ZnCO}_3$	0.001 <sup>15*</sup>	..
Zinc Cyanide	$\text{Zn}(\text{CN})_2$	0.0005 <sup>20</sup>	..
Zinc Hydroxide	$\text{Zn}(\text{OH})_2$	0.00000026 <sup>18</sup>	..

Contd.

Table 2 contd.

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Zinc Oxalate	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$0.00079^{18**}$	..
Zinc Oxide	$\text{ZnO}$	$0.00016^{29}$	..
Zinc Sulphide	$\text{ZnS}$	$0.00069$	..

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1\* insoluble

\*\* temperature in °C

## CHAPTER V

RESULTS & DISCUSSIONS5.1 Ion Exchange

A number of studies have been conducted using ion exchange resins manufactured by various companies. These include, Dowex 50 x 12<sup>23</sup>, Duolite C-20, Tulsin-14, Tulsin-42<sup>20</sup>, KU-2, KB-2<sup>26</sup>, KU-1<sup>28</sup> etc. The efficiency of a resin in removing the required ions is calculated as grams of zinc per litre of the resin. Extraneous materials like dissolved and suspended organics are some times known to foul up the ion exchange resin. The true capacity of a resin sometimes cannot be directly calculated using a raw waste material of unknown composition made up of various extraneous ions. In order to determine the actual capacity of the resin to specifically remove zinc, distilled water with known quantities of zinc sulphate, with an adjusted pH of 2.2 (with sulfuric acid) is used as a synthetic waste. The rate of flow of the influent is normally kept at 1/5<sup>th</sup> of the bed volume/minute as a standard procedure, in this study in conformity with other studies cited in literature<sup>59</sup>. The effluent has been analyzed for concentration of zinc, polarographically and the information is given in Figure 5.

Traces of zinc started appearing in the effluent after a volume of 63 litres of waste has passed through the column. With the analytical technique used the concentration of zinc that can be detected is only after the passage of 63 litres. However there must be slight leakage of zinc after 60 litres, the concentration of which is indicated in the Figure 5. This concentration is in fact in traces, being less than 0.5 mg/l. Based on this experiment the capacity of the resin can be calculated to be 1.44 kg/cft (51.36 grams/litre). The capacity of the resin compared very favourably with many other resins reported in the literature. The experiment was stopped when about 5% leakage of zinc is observed in the effluent.

The resin is rinsed and backwashed, and regenerated. The resin bed is now ready for the next cycle of operation.

Rayon Factory can be said to have two distinct types of wastes as mentioned before. Recovery of zinc will be facilitated if the two wastes are not mixed, but separately treated. Zinc is present in the acidic waste and both from the point of concentration as well as volume, treatment of acidic waste after segregation will be a more economical method. The characteristics of the wastes given before in table 1 on page 15 indicates a typical



acidic rayon waste as compared to the reported characteristics of wastes from other Rayon Industries. The concentration of zinc generally varied from 190 to 375 mg/l.<sup>60</sup> However this range may not represent actual concentrations present at various times since there are only grab samples. It has been cited in literature that the concentration of zinc varies from 190 to 700 mg/l<sup>20</sup>. In the present study the zinc concentration in the waste was about 360 mg/l. The removal of zinc by ion exchange from the acid rayon waste was observed and presented in Figure 6.

Information about specific conductance, concentration of zinc and pH is given in Figure 6. A total volume of 15 litres had passed through, when zinc in detectable concentration appeared in the effluent. The pH of the effluent compared to the influent is depressed to a value of 1.75 due to the displacement of hydrogen ions from the resin by zinc ions as expected. The change in pH is almost concurrent with the appearance of zinc again indicating the decrease in the available sites of adsorption in the resin. The change in specific conductance, even though not as specific as the change in pH still indicates the trend of the performance of the resin.

The initial concentration of zinc is almost  $1\frac{1}{2}$  times that of synthetic waste. The capacity of the resin

based on this experiment is 63.5 gm/litre or 1.8 kg/cft. This figure is more than what has been obtained before with pure zinc sulphate. It may be due to the difference in pH values. The presence of other ion in the raw waste does not seem to have affected the capacity of the resin adversely. Thus the total concentration of dissolved solids has decreased is indicated by the measurement of specific conductance. It would have been more informative if the pH of the waste is adjusted to different values and the removal of zinc observed by the ion exchange. However due to lack of time this could not be attempted.

Removal of zinc is not the only problem to be considered. Since we are interested in the recovery of valuable zinc, the exhausted resin from the previous experiment has been eluted with 5% sulphuric acid. Recovery of zinc is shown in Figure 7. The maximum concentration of zinc in the eluate was with 400 ml of eluant. The percentage of recoverable zinc shown in the same figure indicates that 99% of the total recoverable zinc can be recovered with an eluant volume of 1.5 litres. Beyond this, it does not seem to be economical. The recovered zinc sulphate solution can be sent directly to the spin bath make up tanks without further treatment.

However the total zinc adsorbed by the resin was 9.536 gms per <sup>150</sup>180 ml of resin. The total quantities of zinc recovered during elution was 8.241 gram. From this the recovery efficiency is found to be 86.5%.

It is interesting to observe the performance of the resin used in these experiments. A number of studies using different brand resins have already been discussed in the literature review. Information was not available about many of the resins from available literature to discuss and compare the present study in a detailed way. However, some studies gave valuable material. The capacity to recover the zinc, by some of the resins is presented in table 3, and compared with the capacity of Zeo-karb 225 used in the present study. It seems that the capacity of Zero-karb to recover zinc is higher than those presented in table 2.

The operations with ion exchange are clean, simple and efficient unlike the precipitation process. However, ion exchange columns are expensive to install and require good supervision.

The zinc that is left behind, in the initial removal treatment should not pose a problem in the effluent because of the dilution that is effected by mixing the alkaline and acidic wastes before disposal, Taking that

TABLE 3

FINITE ADSORPTION CAPACITY OF SOME  
RESINS IN HYDROGEN FORM

TYPE OF RESIN	CAPACITY OF RESIN meq/ml
Tulsin-14	0.0930 <sup>20</sup>
Tulsin-42	0.168 <sup>20</sup>
Duolite-C-20	0.2690 <sup>20</sup>
Dowex 50 x 3	0.76 <sup>32</sup>
Zeo-karb 225	1.96

the final concentration of zinc in any of the effluents will be double that of what is obtained here, it would seem that the concentration of zinc will still be well, below the toxic limit for either fish (0.3 mg/l)<sup>5</sup> or for drinking water which is 5 mg/l<sup>7,8</sup>. This is true when the waste water is allowed to join a river or a stream where further dilution is effected.

## 5.2 Chemical Precipitation

Removal of zinc by chemical precipitation has been practiced before. The best removal will be naturally obtained when an insoluble compound of zinc is formed during the chemical reaction. Referring to the table 2, while removal of zinc is possible in the form of arsenide, Ferrocynide, Ortho or Pyro Phosphates, Phosphide and Sulphide. Recovery from this may be difficult. Disposal in these forms is not advisable due to the toxicity of some of these compounds to aquatic organisms, when let out into water courses. Among the compounds that have low solubility are the Carbonate, Cynide, Hydroxide, etc. of zinc.

The least soluble compound seems to be zinc Hydroxide from which recovery of zinc is easier than from the other salts. When the carbonate of zinc was

precipitated it was recovered in the form of sulphide in some cases.<sup>56</sup> The recovery in the form of hydroxide has been attempted using hydroxide of Calcium or Sodium. The use of calcium hydroxide has limitations, when recovery of zinc is contemplated. Calcium hydroxide, with limited solubility contains various impurities and sludge formation is large. It is difficult to precipitate zinc with calcium hydroxide unless a pH value of 9.5 is reached. Excepting the cheapness of calcium hydroxide, the use of lime does not justify for recovery of zinc.

No where in literature the use of Ammonium Hydroxide is indicated. Because of the insolubility of zinc hydroxide, it is felt the recovery of zinc in this form is most useful and best as far as eliminating other impurities are concerned.

The cost of caustic soda compared to liquor ammonia is high (see table 4). However, comparison of efficiencies of Ammonium Hydroxide and Sodium Hydroxide have been attempted and results are given in Figures 8 and 9. The optimum pH for maximum removal with sodium hydroxide is 9.6 while with Ammonium Hydroxide it is 8.6. Excess of Ammonium Hydroxide results in the formation of zinc ammonium hydroxide complex  $[(Zn(NH_3)_6](OH)_2]$  which is

TABLE 4

COST OF CHEMICALS

CHEMICAL	COST IN Rs. PER Kg.
Ammonium Hydroxide (Sp. gr. 0.910)	1.50
Sodium Hydroxide	2.70
Sulphuric Acid	0.70

soluble. So the precipitation of zinc hydroxide with ammonia has to be critically watched for good recovery. Sodium hydroxide forms complex salt with zinc which is also soluble at higher pH values. However the pH of this is beyond 10. This kind of reaction of zinc with anions and cations is due to the amphoteric nature of the metal. The pH control with sodium hydroxide is not too critical compared to ammonia.

The precipitated zinc has good settling properties. In 30 minutes settling time, about 6% sludge volume is obtained. Addition of sulphuric acid will convert the zinc hydroxide to zinc sulphate which can be reused.

The formation of Ammonium Sulfate in the precipitation of zinc hydroxide may not be desirable from disposal point of view because of the toxic nature of ammonium sulphate to aquatic, flora and fauna. However the concentration of ammonium sulphate, when the wastes are mixed with alkaline wastes will be quite low and further dilution in the river water will make it harmless from this action.

In this another point of consideration is the change in pH value of ammonium sulphate water when mixed with alkaline wastes having a pH value of 9.6. There is



some chance of ammonia being stripped out and thus further bringing down of ammonia in the waste water.

Comparison of the cost of chemicals using ammonium hydroxide, sodium hydroxide as well as the sulphuric acid required to produce zinc sulphate are given on page 48.

From comparison of the data, it seems that use of sodium hydroxide is more justified than ammonium hydroxide. More over sodium sulphate is not highly toxic as compared to ammonium sulphate. Another point in favour of sodium hydroxide is its availability in industrial packings and the convenience of handling to the strong smelling ammonia which is difficult to obtain in industrial packings.

An attempt has been made in the study to obtain information on the use of ion exchange resins as well as chemical precipitants for zinc removal and recovery. But the study is not exhaustive by any means. Further work is required to bring out the removal and recovery to be more economical so as to be attractive to the industry.

Approximate Comparative Cost of Chemicals, Used  
for the Recovery of Zinc from Rayon Waste

Quantity of the waste =  $1 \times 10^6$  litres (assumed)

Concentration of Zinc = 360 mg/l

pH = 3.0

(1) Ammonium Hydroxide Method

Chemical	Quantity (Kg)	Cost Rs.
Ammonium Hydroxide		
(Sp. gr. 0.91)	1092	1640
Sulphuric acid	563	394.0
Total Cost		2034.0

(2) Sodium Hydroxide Method

Chemical	Quantity (Kg)	Cost Rs.
Sodium Hydroxide	456	1230
Sulphuric Acid	563	394.0
Total Cost		1624.0

## CHAPTER VI

CONCLUSIONS

1. Ion exchange resin, Zeo-karb 225 is found to be efficient in removing zinc from acidic rayon wastes with an initial concentration of 360 mg/l of zinc.
2. The capacity of the resin is calculated to be 63.5 grams/litre or 1.80 kg/cft.
3. Zinc was recovered from the column by elution with sulphuric acid, and the recovered zinc sulphate could be used by the industry again.
4. Comparison of chemical precipitation with sodium hydroxide and ammonium hydroxide indicated that both are efficient in obtaining 99.5% recoveries.
5. The critical pH for maximum recovery with Ammonium Hydroxide is 8.6 and with Sodium hydroxide is 9.6.
6. It is concluded that the use of sodium hydroxide may be better than the use of ammonium hydroxide due to various reasons.
7. A comparative cost analysis for the chemicals in chemical precipitation is given.
8. The use of polarographic method for estimation of zinc is found to be efficient, accurate and fast.

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